

PATENT SPECIFICATION

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NO DRAWINGS.



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COMPLETE SPECIFICATION.

Polypropylene Composition.

We, SPENCER CHEMICAL COMPANY, a Corporation organized and existing under the laws of the State of Missouri, one of the United States of America, of Dwight Building, City of Kansas City, County of Jackson, State of Missouri, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :—

This invention relates to novel polypropylene compositions. More particularly, it relates to novel polypropylene compositions containing copolymers of ethylene, and to processes related thereto.

Polypropylene is an important and unique thermoplastic resin prepared by the controlled polymerisation of propene, or propylene. Polypropylene is a relatively stiff thermoplastic resin characterised by unusually high tensile strengths, high degrees of elasticity and elongation, and a comparatively low density. Also, the new polymer has high heat resistance temperatures. In view of its advantageous characteristics, polypropylene has obviously been found to be highly useful in a number of increasing applications, for example, in the manufacture of injection molded articles, film, pipe and fibres such as used in ropes requiring high tenacity.

However, notwithstanding the advantageous characteristics of polypropylene, it has been experienced that objects constituted of polypropylene often have unpredictably low impact values, particularly at temperatures relatively low, for example, at temperatures below freezing ($<0^{\circ}\text{C.}$). Furthermore, there has been a desire for an alleviation of the difficulties involved in molding polypropylene as now encountered.

An object of this invention is to provide polypropylene compositions having improved properties, for example improved impact resistance. Another object of this invention is to provide processes for improving polypropylene.

Accordingly, the invention comprises a process of providing polypropylene having improved properties by adding a compatible copolymer, or combination of copolymers, of ethylene and an alkyl acrylate as defined herein to polypropylene and by blending said admixture so as to provide a homogeneous composition.

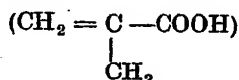
A polymer composition in accordance with this invention comprises polypropylene containing in homogeneous admixture a copolymer or combinations of copolymers of ethylene and an alkyl acrylate. The concentration of the copolymers can vary widely depending upon the intended end use, the particular copolymer employed, and the character of the polypropylene at hand. However, customarily the concentration of ethylene copolymer falling in the range of 5 to 50% on the basis of the total weight of the composition is suitable. A more desired concentration usually is 15 to 35% and a presently preferred concentration is 20 to 30% on the same basis depending again on the copolymer employed, its alkyl acrylate content, the intended end uses, etc.

It is quite surprising, initially speaking, to find that the copolymers of ethylene and an alkyl ester of acrylic acid are compatible with polypropylene, since it has been the experience in the past to observe aversion on the part of polypropylene to incorporation of other polymeric substances, especially at substantial concentrations, e.g., at concentrations exceeding 5%. To illustrate, poly-

ethylene has been observed to have such incompatibilities with polypropylene. Demonstrative of the fact that there is a high degree of compatibility of the copolymers and polypropylene is the high clarity of molded articles thereof.

The polypropylene preparations usable in the formation of the blends of this invention are solids at ordinary temperatures and can vary considerably, for example, in molecular weight and other properties. Suitable polypropylenes can be those such as are marketed for use in film preparation, molding and manufacture of such objects as rope, etc. The polypropylene which has been found preferable can have a melt index, e.g., of about 3.5 to about 6 at a temperature of 250° C. It is preferred to use a polypropylene having a relatively high degree of isotacticity for example, it is customarily desired that the polypropylene have a degree of isotacticity of about 90% or above.

The copolymers of ethylene employed in the preparation of the polypropylene compositions of this invention are formed by the copolymerisation of ethylene with an alkyl acrylate. Alkyl acrylate for the purpose of this invention means an alkyl ester of an acrylic acid, acrylic acid having the definition set forth in *Acrylic Resins*, by Milton B. Horn, p. 15 f., under the title "Monomer Chemistry" wherein an unsubstituted acrylic acid ($\text{CH}_2 = \text{CH}-\text{COOH}$) and simply substituted acrylic acids, for example, those acrylic acids having simple alkyl substituents, such as methacrylic acid:—



are included. Specific alkyl acrylic esters suitable for preparation of the copolymers include the methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tertiary-butyl, hexyl, 2-ethylhexyl, decyl, lauryl and stearyl esters of acrylic or methacrylic acids. It will be obvious to those skilled in the art that the alkyl groups may have simple substituents and such are included within the scope of this invention. It has been found that the unsubstituted alkyl acrylates, i.e., the alkyl esters of simple acrylic acid are preferred. Among the esters of unsubstituted acrylic acid, the presently preferred one is the methyl acrylate.

It has been found that the copolymers which contain in the range of 4 to 60% of alkyl acrylate groups by weight are suitable for use in the compositions. A preferred per cent of alkyl acrylates in the copolymers is in the range of 6 to 30%, customarily 15 to 25% being the presently most preferred percentage range. The difference in molecular weight of the alkyl acrylates must be borne

in mind in consideration of the content of alkyl acrylate in the copolymers, particularly since the number of alkyl acrylate groups apparently exceeds the weight per cent quantity as a reliable measure of the amount of a particular alkyl acrylate predictably preferred to be present. It is preferred to have a high uniformity of distribution of the alkyl acrylate groups among the copolymer chains.

It has been found desirable in the preparation of the preferred copolymers for use in this invention to follow a continuous type procedure employing a reactor of the autoclave type. In the above reaction process, the preferred type of reactor has a high ratio of the height to the diameter of the reactor, a suitable height to diameter ratio being around 10 to 15. In this procedure, a stream of ethylene under high pressure is introduced into the reaction chamber simultaneously with an alkyl acrylate. The introduction of the two reactants is made in such a manner so as to insure a substantially uniform mixture of the ethylene and the alkyl acrylate when the two reactants enter the reaction zone of the reactor. Customarily, the most convenient and reliable manner to insure such a simultaneous introduction of the two reactants on entrance into the reaction zone is to introduce them into the reactor by means of a common inlet as a mixture. However, any other means of introduction of the two reactants is satisfactory that will provide the desired end results. A feed having a relatively low percentage of alkyl acrylate is generally employed in the production of the preferred copolymers, usually not in excess of about 5% by weight of alkyl acrylate. It has been found advisable to regulate the reaction stream in such a manner that a relatively small per cent of the introduced comonomers of ethylene and alkyl acrylate are consumed in a single pass through the reactor. The unreacted ethylene of the reactor discharge is recovered and is recirculated for incorporation in the comonomer feed.

The pressure and temperature conditions which are preferably employed correspond in general to those which have been found to function adequately in polyethylene production. Pressure is desirably maintained within the reactor during the formation of the copolymer in the range of about 10,000 to about 40,000 psi, preferably between 15,000 and 25,000 psi. In respect to the temperature it is desirably maintained in the range of about 200 to about 500° F., preferably within the range of about 300 to 400° F. It has been found suitable to feed the comonomers into the reactor under most of the conditions at a rate in the range of about 200 to about 800 lb/hr/cu. ft. of reactor volume.

During the reaction it has been found desirable to provide a vigorous mixing within

the reactor by means of, e.g., an agitator rotating at a relatively high rate. It is desirable to have an agitator of such a character which will provide some back-mixing in the reaction zone.

In the preparation of the copolymers, a catalyst or a polymerization initiator is employed, preferably the free radical type such as those highly effective ones which are presently available. Additionally, it is desirable to maintain the oxygen level within the reactor at minimal level. In view of the fact that it is desirable to keep the oxygen within the reactor at a relatively low level, the use of air or oxygen in preferred preparative procedures is of course precluded. Representative suitable catalysts employable in the preferred procedures include organic peroxides such as lauroyl peroxide, ditertiary-butyl peroxide, caprylyl peroxide, tertiary-butyl perbenzoate and tertiary-butyl peracetate and azo initiators such as α, α' -azobisisobutyronitrile, β, β' -azobisethylpropionate and β, β' -azobisethylisobutyrate. The initiator can be injected into the reactor using a vehicle, e.g., benzene and/or mineral oil or other suitable solvents as a carrier. About 50 to 20,000 ppm, and generally 100-250 ppm of initiator in the reaction mixture, based on the ethylene feed weight and depending on the specific initiator, are usually adequate for the process. In the introduction of the initiator, it must be borne in mind that as a general consideration temperature can be regulated at least in part by controlling the initiator introduced.

Other procedures can be used to prepare alkyl acrylate copolymers utilizable in the preparation of the polypropylene blends of this invention, e.g., certain controlled batch and semi-continuous procedures. Currently, however, the polymers provided by the above described procedure or simple variations therefrom have been found to provide the preferred copolymers.

The molten polymer produced on discharge is collected in the customary manner and is extruded as a molten belt into a water bath for cooling. The cooled, solidified belt of the provided copolymer of ethylene and the alkyl acrylate then is removed from the water bath as by a conveyor and is cubed or severed into other convenient forms for the final compounding of the polypropylene compositions provided hereby.

The blends can be prepared following mixing and blending procedures well known to those skilled in the thermoplastic compounding art. For example, cubes of polypropylene and cubes of one of the ethylene-alkyl acrylate copolymers can be thoroughly mixed preliminarily. The mixed cubes can then be thoroughly blended by using a Banbury mixer, or preferably using a compounding extruder type of mixer, to blend uniformly

the mixture, following conditions and regimens well known to the art.

The blends provided above have wide applicability. They are useful in providing a great number of consumer items which are customarily manufactured of thermoplastics such as polyethylene or polypropylene, such items being prepared using standard molding equipment and procedures such as compression molding or injection molding and other applicable processes for the preparation of film, pipe, fibers and the like.

Additives customarily employed for incorporation into polypropylene preparations such as coloring agents, stabilizers, lubricants, ultra-violet desensitizers, anti-block agents, and the like can be utilized in the final preparations. The selection and the procedures of incorporation of such additives can be conducted in accordance with principles and procedures within the knowledge and skill of the art.

Standard tests applicable to pure polypropylene preparations or simple modifications thereof are employed to evaluate quantitatively such common properties as melt index, moldability, impact values at various temperatures, stiffness values, and heat resistance points and the like on the compositions of this invention.

The following examples are provided in illustration of the compositions of this invention. Examples 1 to 8 illustrate methods of preparing copolymers for use in polymer admixtures in accordance with the invention.

EXAMPLE 1.

Preparation of Ethylene-Methyl Acrylate Copolymers.

The reactants are fed through a single entry into a high pressure, agitated autoclave reactor of a type used in polyethylene production, at a ratio of 2 parts of methyl acrylate to 98 parts of ethylene by weight and at a rate of about 500 lb/hr/cu. ft. of reactor volume. The reaction feed employed has low moisture and oxygen contents. Lauroyl peroxide is injected as the free radical initiator in a benzene-mineral oil vehicle at a rate of about 750 ppm on the basis of the weight of feed. The reaction is conducted at a pressure maintained at about 17,500 psi. The temperature is kept in the range of 300° F. to about 430° F., for the most part controlled at around 360° F. The reactor is equipped with a longitudinal agitator which is rotated at a rate of about 250 rpm.

The unconsumed reactants along with the formed copolymer are discharged from the reactor in a conversion of from 15 to 20% of the total weight of the reactants to the copolymer. Nearly all of the unpolymerized discharge of reactants is ethylene. It is recovered from the molten copolymer by

means of the customary separator vessels and circulated for re-use.

The separated molten polymer is then extruded as a belt or ribbon into a water bath for solidification. The solidified copolymer of ethylene and methyl acrylate is severed into cubes for blending.

The copolymer has the following properties: a content of 15% methyl acrylate by weight as determined by infra-red analysis, a melt index of 1.72, a density of 0.9365, and a Vicat softening point of 71° C.

EXAMPLE 2.

Preparation of an Ethylene-Methyl Acrylate Copolymer.

Following the procedure of Example 1, an ethylene-methyl acrylate copolymer is prepared employing the following conditions: Feed constitutes 3.3 parts of methyl acrylate and 96.7 parts of ethylene by weight at a rate of about 500 lb/hr/cu. ft. of reactor volume; reactor temperature maintained in the range of 300° F. to 410° F. and controlled at around 352° F., the reactor pressure maintained at about 20,200 psi, and about 350 ppm on the basis of feed weight of lauroyl peroxide introduced as initiator.

The provided ethylene-methyl acrylate copolymer has a content of 25% methyl acrylate by weight, as determined by infra-red analysis, has a melt index of 1.81, has a density of 0.9447 and has a Vicat softening point of 47° C.

EXAMPLE 3.

Preparation of an Ethylene-Methyl Acrylate Copolymer.

Following the procedure of Example 1, an ethylene-methyl acrylate copolymer is prepared employing the following conditions: Feed constitutes 3.3 parts of methyl acrylate and 96.7 parts of ethylene by weight at a rate of about 500 lb/hr.; reactor temperature maintained in the range of 290° F. to 410° F., and for the most part controlled at around 350° F., the reactor pressure maintained at about 20,200 psi, and about 350 ppm on the basis of feed weight of lauroyl peroxide, introduced as initiator.

The provided ethylene-methyl acrylate copolymer has a content of 25% methyl acrylate by weight as determined by infra-red analysis, has a melt index of 0.34, has a density of 0.9443 and has a Vicat softening point of 52° C.

EXAMPLE 4.

Preparation of an Ethylene-Methyl Acrylate Copolymer.

Following the procedure of Example 1, an ethylene-methyl acrylate copolymer is prepared employing the following conditions: Feed constitutes 2.2 parts of methyl acrylate and 97.8 parts of ethylene by weight at a rate

of 600 lb/hr/cu. ft. of reactor volume; reactor temperature maintained in the range of 315° F. to 400° F. and for the most part controlled at around 360° F., the reactor pressure maintained at about 16,800 psi and about 350 ppm on the basis of feed weight of lauroyl peroxide employed as initiator.

The provided ethylene-methyl acrylate copolymer has a content of 11% methyl acrylate by weight, has a melt index of 2.45, has a density of 0.9305, and has a Vicat softening point of 80° C.

EXAMPLE 5.

Preparation of an Ethylene-Methyl Methacrylate Copolymer.

Following the procedure of Example 1, an ethylene-methyl methacrylate copolymer is prepared employing the following conditions: Feed constitutes 2 parts of methyl methacrylate and 98 parts of ethylene by weight; reactor temperature maintained in the range of 240° F. to 340° F. and for the most part controlled at around 335° F., the reactor pressure maintained at about 22,500 psi and about 400 ppm on the basis of feed weight of caprylyl peroxide employed as initiator.

The provided ethylene-methyl methacrylate copolymer has a content of 5.3% methyl methacrylate by weight as determined by infra-red analysis, has a melt index of 0.55, has a density of 0.9274, and has a Vicat softening point of 70.5° C.

EXAMPLE 6.

Preparation of an Ethylene-Butyl Methacrylate Copolymer.

Following the procedure of Example 1, an ethylene-butyl methacrylate copolymer is prepared employing the following conditions: Feed constitutes 3 parts of butyl methacrylate and 97 parts of ethylene; reactor temperature maintained in the range of 300° F. to 350° F. and for the most part controlled at around 330° F., the reactor pressure maintained at about 21,000 psi, and about 400 ppm on the basis of feed weight of caprylyl peroxide employed as initiator.

The provided ethylene-butyl methacrylate copolymer has a content of about 8.9% butyl methacrylate by weight as determined by infra-red analysis, has a melt index of 4.45, has a density of 0.9219 and a Vicat softening point of 52° C.

EXAMPLE 7.

Preparation of an Ethylene-Butyl Acrylate Copolymer.

Following the procedure of Example 1, an ethylene-butyl acrylate copolymer is prepared employing the following conditions: Feed constitutes 1.4 parts of butyl acrylate and 98.6 parts of ethylene by weight; reactor temperature maintained in the range of 300° F. to 350° F. and for the most part

controlled at around 324° F., the reactor pressure maintained at about 18,000 psi, and about 300 ppm on the basis of feed weight of caprylyl peroxide employed as initiator.

The provided ethylene-butyl acrylate copolymer has a content of 4.2% butyl acrylate by weight as determined by infra-red analysis, has a melt index of 2.87, has a density of 0.9210, and a Vicat softening point of 75.8° C.

EXAMPLE 8.

Preparation of Ethylene-Alkyl Acrylate Copolymers.

Other ethylene-alkyl acrylate copolymers employable in the compounding of the polypropylene compositions of this invention are prepared following the procedure of Example 1 and using the specific conditions as set forth in the following table:—

Lot.	Copolymer.*	Feed (parts by weight).	Control temp. (° F.).	Pressure (psi).	Alkyl acrylate (% by wt.).
A	eth-stearyl methacrylate	99, eth ; 1 stearyl MA	274	16,500	16.5
B	eth-stearyl acrylate	99, eth ; 1 stearyl A	290	17,200	16
C	eth-2-methyl-hexyl methacrylate	97.25, eth ; 2.75 2-methyl-hexyl methacrylate	330	19,250	9.2
D	eth-methyl methacrylate	97.2, eth ; 2.8, methyl methacrylate	360	21,500	9.4

* eth—abbreviation for ethylene
MA—abbreviation for methacrylate.
A—abbreviation for acrylate.

EXAMPLE 9.

Preparation of Copolymer-Containing Polypropylene Compositions.

Quantities of cubed polypropylene having an isotacticity figure of about 90% and a melt index at 250° C. of 3.5 are added to quantities of cubed copolymers prepared as described in the above examples in a manner and in quantities as set forth in the following table. The combined polymer cubes are mixed to provide an even distribution. The mixtures of the cubes are blended by using a Banbury mixer. A compounding extruder mixer is

used for the blending in lieu of the Banbury mixer at times. Customarily in the use of a Banbury mixer, the mixing is carried on for a 2 to 5 minute period of time maintaining the temperature at about 350° F., whereas in the use of a compounding extruder a stock temperature range of 375—500° F., are employed.

The blended preparations of polypropylene are employed following customary procedures for the formation of molded articles, films and other commercial articles.

Composition Number.	Copolymer.	Copolymer parts by wt.	Polypropylene parts by wt.
1	eth-methyl acrylate (Ex. 1)	15	85
2	"	25	80
5 3	eth-methyl acrylate (Ex. 2)	25	75
4	"	35	65
5	eth-methyl acrylate (Ex. 3)	10	90
6	"	25	75
7	eth-methyl methacrylate (Ex. 5)	20	80
10 8	"	30	70
9	eth-butyl methacrylate (Ex. 6)	25	75
10	eth-methyl methacrylate (Ex. 8-D)	25	75
11	"	50	65
15 12	eth-methylhexyl methacrylate (Ex. 9-C)	25	75
13	eth-stearyl methacrylate (Ex. 9-B)	25	75
14	eth-butyl acrylate	25	75

WHAT WE CLAIM IS:—

1. A polymer composition comprising in a homogeneous admixture polypropylene and a compatible copolymer, or combination of copolymers, of ethylene and alkyl acrylate as defined herein.

2. A composition as claimed in Claim 1, in which the copolymer is prepared in highly uniform form, and is the product of a continuous process in which ethylene and an alkyl acrylate are introduced into and agitated in a reactor.

3. A composition in accordance with Claim 1, wherein the alkyl acrylate employed in the copolymer formation is an ester of unsubstituted acrylic acid.

4. A composition in accordance with Claim 1 wherein the alkyl acrylate employed in the copolymer formation is an ester of methacrylic acid.

5. A polymer composition as claimed in any of the preceding claims wherein the concentration of said copolymer is in the range of 5 to 50% on the basis of total polymer weight of the composition.

6. A composition in accordance with Claim 5 wherein the concentration of the copolymer is in the range of 15 to 35% on the basis of total polymer weight of the composition.

7. A composition in accordance with Claim 5 wherein the concentration of the copolymer is in the range of 20 to 30% on the

basis of total polymer weight of the composition.

8. A composition in accordance with Claim 5 wherein the copolymer employed consists of from 4 to 60% by weight of alkyl acrylate groups.

9. A polymer composition as claimed in any of the preceding claims wherein the alkyl acrylate is methyl acrylate and the concentration of said copolymer is in the range of 15 to 35% on the basis of total polymer weight of the composition.

10. A composition in accordance with Claim 8 wherein the copolymer employed consists of from 6 to 30% by weight of methyl acrylate groups.

11. A composition in accordance with Claim 8 wherein the concentration of copolymer is in the range of 20 to 30% on the basis of total polymer weight of the composition and wherein said copolymer employed consists of from 6 to 30% by weight of methyl acrylate groups.

12. A process of providing polypropylene having improved properties by adding a compatible copolymer, or combination of copolymers, of ethylene and an alkyl acrylate as defined herein to polypropylene and by blending said admixture so as to provide a homogeneous composition.

13. A process in accordance with Claim 12, wherein the copolymer is prepared in highly uniform form and is the product of a

- continuous process in which ethylene and an alkyl acrylate are introduced into and agitated in a reactor.
14. The process in accordance with Claim 5 12 wherein said alkyl acrylate is an ester of unsubstituted acrylic acid.
15. A process in accordance with Claim 12 wherein said alkyl acrylate is an ester of methacrylic acid.
- 10 16. A process in accordance with Claim 12 wherein the copolymer is added in an amount to provide a final concentration of said copolymer in the range of 5 to 50% on the basis of total polymer weight of the composition.
- 15 17. A process in accordance with Claim 16 wherein the copolymer is added in an amount to provide a final concentration of said copolymer in the range of 15 to 35% on the basis of the total polymer weight of the composition.
- 20 18. A process in accordance with Claim 17 wherein the copolymer is added in an amount to provide a final concentration of said copolymer in the range of 20 to 30% on the basis of the total polymer weight of the composition.
- 25 19. A process in accordance with Claim 16 wherein said copolymer consists of from 4 to 60% by weight of alkyl acrylate groups.
20. A process in accordance with Claim 12 wherein said alkyl acrylate comprises methyl acrylate in an amount to provide a final concentration of said copolymer in the range of 15 to 35% on the basis of total polymer weight of the composition.
21. A process in accordance with Claim 20 wherein said copolymer consists of from 6 to 30% by weight of methyl acrylate groups.
22. A process in accordance with Claim 20 wherein said methyl acrylate is added in an amount to provide a final concentration of said copolymer in the range of 20 to 30% on the basis of total polymer weight of the composition, and said copolymer consists of from 6 to 30% by weight of methyl acrylate groups.
23. The processes of providing propylene compositions as claimed in any of Claims 12 to 22, and substantially as described herein.
24. Propylene compositions as claimed in any of Claims 1 to 11 and substantially as described herein.
- HASELTINE, LAKE & CO.,
Chartered Patent Agents,
28 Southampton Buildings,
Chancery Lane,
London, W.C.2.
Agents for the Applicants.

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